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Hydrogen fatigue-resisting carbon steels

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Abstract

Hydrogen fatigue-resistant carbon steels that show dramatically reduced hydrogen-induced fatigue crack growth acceleration were successfully produced, as results of combining the addition of carbide-forming elements and the refinement of ferrite crystal grains. When carbon steels with the carbide-forming elements Vanadium (V), Titanium (Ti) and Niobium (Nb) added individually were caliber-rolled at 833 K, fine carbides (VC, TiC or NbC) were precipitated and the ferrite crystal grain size became less than or equal to 1 μm.

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Keywords: hydrogen embrittlement; fatigue; crack growth; carbon steels; ultrafine-grained microstructure; carbide-forming elements

1. Introduction

To protect the Earth's environment and prevent the depletion of fossil fuel resources, hydrogen energy systems such as fuel cell vehicles and stationary fuel cells, and infrastructures such as hydrogen stations and hydrogen pipelines, is being developed. However, in Japan, due to hydrogen embrittlement of metals, only two types of metals, Type316L austenitic stainless steel and JIS-6061-T6 (UNS No. A96061) aluminum alloy, are allowed to be used as material for high-pressure hydrogen storage tank liners and valves for fuel cell vehicles [1]. Type316L and A96061 have been selected as materials resistant to hydrogen embrittlement. Type316L is commonly used for pipes and valves for hydrogen stations. However, both Type316L and A96061 are costly. If carbon steel resistant to hydrogen degradation of fatigue properties is developed, cheaper and safer fuel cell vehicles and hydrogen stations can be achieved.

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This study shows that carbon steels that demonstrate dramatically reduced hydrogen-induced fatigue crack growth acceleration can be successfully produced by combining the addition of carbide-forming elements, Vanadium (V), Titanium (Ti), Niobium (Nb), and the refinement of ferrite crystal grains.

2. Experimental Procedure

2.1. Materials

The materials used in this study was a low carbon steel (0.05C-0.30Si-1.5Mn in mass%). This carbon steel is named SO5C here. Three types of carbon steels with carbide-forming elements, 0.25mass% Ti, 0.27mass% V and 0.45mass% Nb, added individually to SO5C, were prepared. These carbon steels are named Ti-SO5C, V-SO5C, and Nb-SO5C. The last specimen, used for comparison, was a medium carbon steel, JIS-S45C (0.47C-0.18Si-0.63Mn in mass%).

When preparing SO5C, Ti-SO5C, V-SO5C, and Nb-SO5C materials, to refine ferrite crystal grains, 80-mm bars were produced and subjected to a temperature of 1443 K for one hour, air cooled, caliber-rolled at 833 K to a 95% reduction, and then water cooled, based on the process and heat treatment conditions used in the previous report [2]. The diameter of the bars after caliber-rolling was 17 mm. The tensile strength of these fine-grained steels was 924 MPa in SO5C, 790 MPa in Ti-SO5C, 937 MPa in V-SO5C, and 883 MPa in Nb-SO5C. To compare the effect of hydrogen on fatigue properties between the fine-grained steels and the comparison steel JIS-S45C at the same level of tensile strength, JIS-S45C was quenched in water at 1118 K for half an hour and tempered in water at 823 K for one hour. The tensile strength of JIS-S45C was 906 MPa.

Figure 1 shows a transmission electron microscopy (TEM) image of the microstructure of the fine-grained steel Ti-SO5C. It reveals that the ferrite crystal grain size is less than or equal to 1 μm. The ferrite crystal grain size of other fine-grained steels (SO5C, V-SO5C and Nb-SO5C) was also not more than 1 μm. A TEM-EDX analysis of the replica specimens showed that TiC, VC and NbC, respectively, were formed in the Ti-SO5C, V-SO5C and Nb-SO5C fine-grained steels with carbide-forming elements individually added, and confirmed that the particle size of their carbides was 20 to 200 nm.

Fig. 1. TEM image of the fine-grained Ti-S05C steel.

2.2. Preparation of hydrogen-induced specimens for fatigue tests

Smooth and notched-bar specimens were prepared for axial-load fatigue testing by machining to 17 mm in diameter the SO5C, Ti-SO5C, V-SO5C and Nb-SO5C bars produced by caliber-rolling. The test section of the smooth specimen was 8 mm in diameter and 16 mm long. The notched specimen was prepared by making a 0.7 mm-deep V-shaped circumferential notch in the center of the test section of the smooth specimen. The stress concentration factor, Kt, of the notch was 3.7. Notched plate specimens (12 mm wide and 10 mm thick with a 1.5 mm-deep V-notch) for fatigue crack growth testing were also fabricated from the 17 mm-diameter bars. For fatigue crack growth testing, 50 mm-wide, 10 mm-thick compact tension (CT) test specimens were used.

The specimens were immersed in a 20mass% ammonium thiocyanate aqueous solution at 313 K and charged with hydrogen. Since the hydrogen impregnated in the specimens for hydrogen measurement for each material was saturated in 20 hours, the fatigue test specimens were immersed in the solution for 48 hours.

Immediately after completion of immersion in the ammonium thiocyanate aqueous solution, the amount of hydrogen impregnated in the bar specimens for hydrogen measurement was measured using a gas chromatography-type thermal desorption analyzer (TDA). Since very little hydrogen was released at temperatures above 623 K, the cumulative amount of hydrogen released until the temperature reached 623 K was used as the hydrogen storage amount.

2.3. Hydrogen-induced fatigue crack propagation tests

Axial-load testing (fatigue life test) was performed at a stress ratio of R = -1 and test frequencies of f = 0.2, 2 or 30 Hz. Fatigue crack growth tests of fine-grained steel were performed using notched plate specimens under bending load, based on the test method developed by Kikukawa et al. [3]. Fatigue crack growth tests of the comparison material, S45C, were performed using CT test specimens. For high-frequency testing at 30 Hz, two test methods were used: a method in which ΔK was decreased at R = 0.1 (a constant R/decreasing ΔK test) and a method in which ΔK is decreased at constant maximum load P_{max} (a constant P_{max}/decreasing ΔK test). The test at a constant load amplitude (constant ΔP test) also was performed at R = 0.5, and f = 0.2 and 2 Hz to investigate the effect of the test frequency on the fatigue crack growth properties of the hydrogen-charged specimens.

The effect of hydrogen on fatigue properties has been reported to be greater on crack growth than on crack initiation [4-6]. In addition, it is known that in the relationship between the stress amplitude, σ_a, and the number of cycles to failure, N_f, (S-N properties) obtained in an fatigue test of smooth-bar specimens, the number of cycles to fatigue crack initiation, accounts for the most of the number of cycles to failure. In this study, S-N properties of smooth-bar specimens for quenched-tempered JIS-S45C were obtained to investigate the effect of hydrogen on fatigue crack initiation life. The S-N properties obtained were nearly the same for the hydrogen-charged and hydrogen-free specimens at the test frequencies of f = 0.2, 2 and 30 Hz. This shows that hydrogen has little effect on fatigue crack initiation.

3. Results and Discussion

Figure 2 shows typical examples of the S-N properties of V-SO5C, the V-added fine-grained steel and JIS-S45C, the comparison quenched-tempered steel, obtained with notched-bar specimens. The number attached to each plot for the hydrogen-charged specimen denotes the residual hydrogen content (in massppm). The effect of the test frequency on the S-N properties of the hydrogen-charged notched specimens was investigated on the high-stress (σ_a = 350 MPa) and low-life side with less hydrogen release from the specimen.

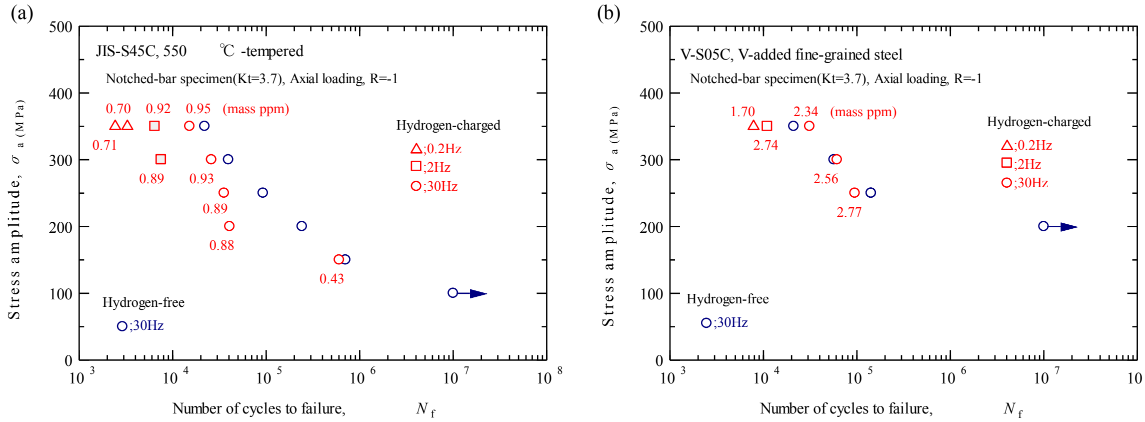

Fig. 2. S-N curves of hydrogen-charged and hydrogen-free specimens. (a) For the tempered JIS-S45C steel. (b) For the fine-grained V-S05C steel with carbides.

The number of cycles to failure of the hydrogen-charged specimens of the quenched-tempered steel JIS-S45C in Fig. 2(a) decreased as the test frequency decreased from 30 to 0.2 Hz at a stress amplitude of σ_a = 350 MPa. The ratio of the number of cycles to failure of the hydrogen-charged specimens $(N_f)_H$ to the number of cycles to failure of the hydrogen-free specimens N_f at 0.2 Hz was $(N_f)_H/N_f \approx 1/10$. In contrast to the smooth-bar specimens, most of fatigue life is spent by the fatigue crack growth in the notched-bar specimens, where N_f is the number of cycles to failure of the hydrogen-free specimens and $(N_f)_H$ is the number of cycles to failure of the hydrogen-charged specimens.

This indicates that in JIS-S45C, hydrogen accelerated fatigue crack growth 10-fold. The fatigue life of the hydrogen-charged specimens of the V-added fine-grained steel V-SO5C in Fig. 2(b) decreased as the test frequency decreased, but the extent of decrease was smaller than in JIS-S45C. The ratio of the number of cycles to failure of the hydrogen-charged specimens $(N_f)_H$ to the number of cycles to failure of the hydrogen-free N_f at 0.2 Hz was $N_f/(N_f)_H \approx 10$ for JIS-S45C and $N_f/(N_f)_H \approx 2$ for V-SO5C. We therefore conclude that addition of the carbide-forming element V and the refinement of ferrite crystal grains reduce hydrogen-induced fatigue crack growth acceleration. This effect was more pronounced in the fatigue crack growth tests.

Figure 3 shows the relationship between the fatigue crack growth rate da/dN and the stress intensity factor range ΔK. The number attached to the data for the hydrogen-charged specimens denotes the residual hydrogen content after the test. For JIS-S45C in Fig. 3(a), the fatigue crack growth rate of the hydrogen-charge specimens was accelerated at higher values of ΔK, more than 10 times faster than that of the hydrogen-free specimens, regardless of the three test methods: the constant R/decreasing ΔK method (R = 0.1), the constant P_{max}/decreasing ΔK method (R = 0.5 to 0.92), or the constant ΔP method (R = 0.5). For V-SO5C, the V-added fine-grained steel in Fig. 3(b), the fatigue crack growth rate was nearly the same for both the hydrogen-charged and hydrogen-free specimens.

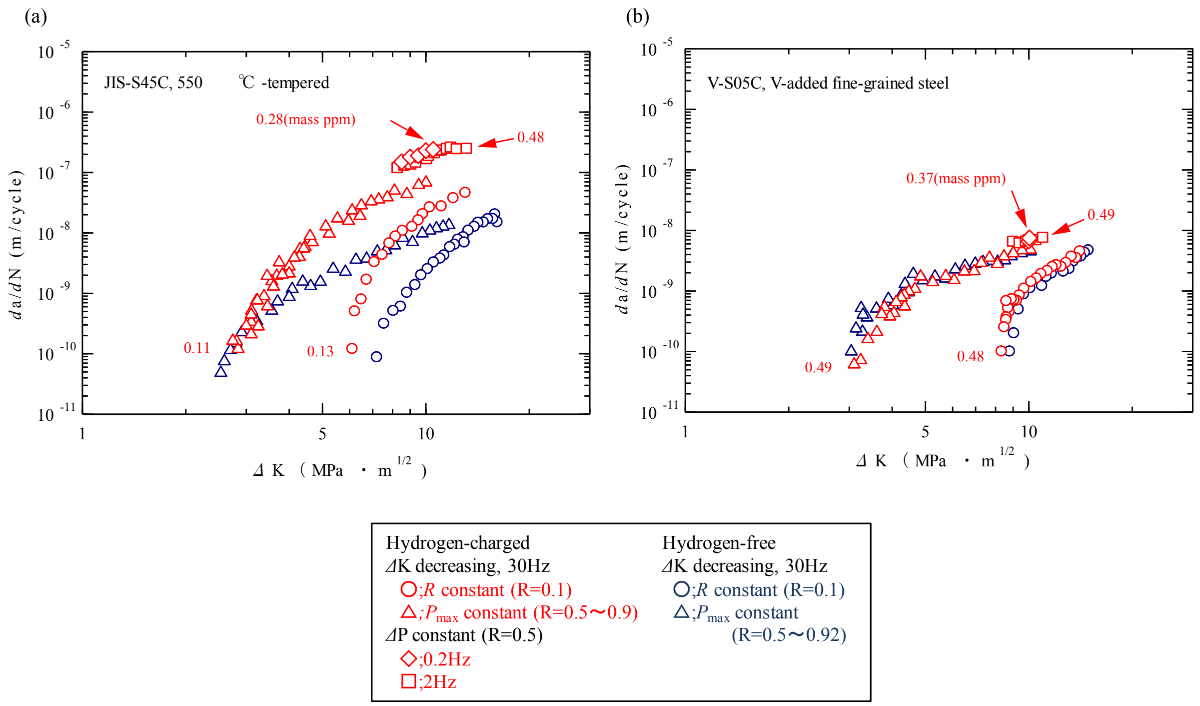

Fig. 3. *da/dN*-ΔK curves of hydrogen-charged and hydrogen-free specimens. (a) For the tempered JIS-S45C steel. (b) For the fine-grainedV-S05C steel with carbides.

Figure 4 shows the results for all the carbon steels tested in this study. Figure 4(a) shows the relationship between the fatigue life ratio $N_f/(N_f)_H$ and the test frequency f at σ_a = 350 MPa obtained with the notched specimens. The reason for using $N_f/(N_f)_H$ is to allow easier comparison with the fatigue crack growth rate ratio, $(da/dN)_H/(da/dN)$, shown in Fig. 4(b). Figure 4(b) shows the relationship between the fatigue crack growth rate ratio $(da/dN)_H/(da/dN)$ and the test frequency f at ΔK = 10 MPa·m$^{1/2}$, where $(da/dN)_H$ is the fatigue crack growth rate of the hydrogen-charged specimens and (da/dN) is the fatigue crack growth rate of the hydrogen-free specimen. For JIS-S45C, the comparison tempered martensitic steel, $N_f/(N_f)_H \approx 10$ and $(da/dN)_H/(da/dN) \approx 25$ at f = 0.2 Hz. For SO5C, the fine-grained steel without carbide-forming elements, both $N_f/(N_f)_H$ and $(da/dN)_H/(da/dN)$ were about 5 at f = 0.2 Hz. This shows that the hydrogen-induced fatigue crack growth acceleration can be reduced only by refining the ferrite crystal grains. For the carbide-forming element-added fine-grained steels, both $N_f/(N_f)_H$ and $(da/dN)_H/(da/dN)$ were not more than 2 at f = 0.2 Hz.

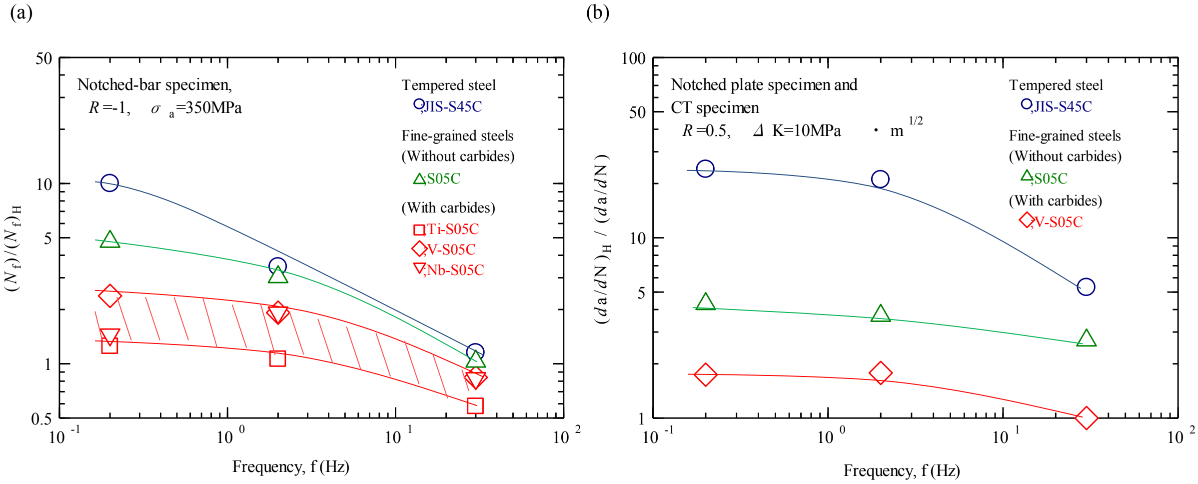

Fig. 4. Summary of hydrogen effect on fatigue life N_f and fatigue crack growth rate da/dN. (a) Plot of $N_f/(N_f)_H$ versus frequency. (b) Plot of $(da/dN)_H/(da/dN)$ versus frequency.

4. Conclusions

It is concluded that hydrogen fatigue-resisting carbon steel that can nearly completely prevent the hydrogen-induced fatigue crack growth acceleration can be produced by adding carbide-forming elements and refining ferrite crystal grains.

Acknowledgements

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